

REACTIONS OF METAL CARBONYL CLUSTER COMPLEXES WITH MULTIDENTATE PHOSPHINE LIGANDS; PREPARATION OF 1,1-BIS(DIPHENYLPHOSPHINO)ETHENE DERIVATIVES, AND THE X-RAY CRYSTAL STRUCTURES OF $\text{Fe}(\text{CO})_3(\text{dppee})$ AND $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ ($\text{dppee} = \text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$)

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(Received March 5th, 1986)

Summary

A number of metal cluster carbonyl complexes containing the 1,1-bis(diphenylphosphino)ethene (dppee) ligand have been prepared and characterised, as have the mononuclear iron complexes $\text{Fe}(\text{CO})_4(\text{dppee})$ and $\text{Fe}(\text{CO})_3(\text{dppee})$. The crystal structures of $\text{Fe}(\text{CO})_3(\text{dppee})$ and $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ have been determined.

Introduction

Our interest in the stabilisation of metal cluster complexes by multidentate phosphine ligands [1] and in the preparation of phosphinated-silica-supported metal cluster complexes [2] led us to investigate the ligand 1,1-bis(diphenylphosphino)ethene (dppee), in which the C=C double bond in the backbone of the ligand allows the possibility of the creation of functionalised diphosphines.

The dppee ligand was first reported in 1982 [3,4], but very few metal complexes containing the ligand have been synthesized. Complexes containing dppee in both chelating and bridging coordination modes have been reported, however. Thus, in $\text{M}(\text{CO})_4(\text{dppee})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [4–6] the ligand chelates to the metal atom, while in the complexes $\text{ClAu}(\mu\text{-dppee})_2\text{AuCl}$ and $\text{ClAu}(\mu\text{-dppee})\text{AuCl}$ [7] the ligand bridges two Au atoms. The crystal structure of $\text{ClAu}(\mu\text{-dppee})_2\text{AuCl}$ [7] is the only structure determination of a complex containing a dppee ligand, although the crystal structure of the free dppee molecule has been determined [8].

It has been found that coordination of dppee leads to activation of the C=CH₂ double bond [6,7]. For example, in complexes of the type $\text{M}(\text{CO})_4(\text{dppee})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), the double bond readily undergoes Michael-type additions [6]. A similar activation is achieved by quaternisation of the phosphine with CH₃I or CH₃OSO₂F

[9,10]. This activation prompted us to investigate metal cluster carbonyls containing the dppee ligand, with a view to using the $C=CH_2$ double bond of the coordinated ligand as a site for attachment of the ligand to inorganic oxide or organic polymer supports. The results of these investigations will be reported in a subsequent paper. This paper reports on the preparation and characterisation of the initial complex, together with the crystal structures of two of the complexes, $Fe(CO)_3(dppee)$ and $Os_3(CO)_{10}(dppee)$, in which the dppee ligand is chelating to a single metal atom, and bridging a metal-metal bond, respectively.

Experimental

IR spectra were recorded in CH_2Cl_2 solution in 0.5 mm NaCl cells on a Perkin-Elmer 681 spectrometer. NMR spectra were recorded on a Bruker WM250 instrument. Mass spectra were obtained using Fast Atom Bombardment on a VG7070E instrument using 2,4-di-*t*-butylphenol-glycerol suspensions. All reactions were carried out under nitrogen using dry, degassed solvents and conventional Schlenk-line techniques. The metal carbonyl $Ru_3(CO)_{12}$ [11] and the ligand dppee [3] were prepared by published methods, and $Fe(CO)_5$ (Aldrich) and $Os_3(CO)_{12}$ (Strem Chemicals) were used as received. Microanalyses were carried out by Elemental Micro-Analysis Ltd., (Devon).

Reaction of $Fe(CO)_5$ with dppee

To a solution of dppee (1.53 g, 3.86 mmol) and $Fe(CO)_5$ (0.5 cm³, 3.86 mmol) in THF (70 cm³) was added dropwise a solution of $Me_3NO \cdot 2H_2O$ (0.43 g, 3.86 mmol) in methanol (20 cm³). The resultant red solution was refluxed for 3 h, and then evaporated to dryness. The residue was heated to reflux temperature in heptane (200 cm³) from 3 h, in air, the hot solution was filtered, and the filtrate cooled to 0°C. Red crystals of $Fe(CO)_3(dppee)$ (1.07 g, 52%) were obtained. These were filtered off, and the filtrate was left at 0°C for several days when orange crystals of $Fe(CO)_4(dppee)$ were obtained (0.52 g, 24%). Microanalysis: $Fe(CO)_3(dppee)$, Found: C, 61.82; H, 3.99; P, 10.69; Cl, 5.15. $C_{29}H_{22}O_3P_2Fe \cdot 0.4CH_2Cl_2$ calcd.: C, 61.89; H, 4.00; P, 10.88; Cl, 4.98%. $Fe(CO)_4(dppee)$, Found (calcd.): C, 63.70 (63.80); H, 4.07 (3.94); P, 10.41 (10.98)%.

Preparation of $Ru_3(CO)_{10}(dppee)$

$Ru_3(CO)_{12}$ (0.50 g, 0.78 mmol) and dppee (0.31 g, 0.79 mmol) in THF (50 cm³) were warmed to 40°C. To this solution was added 3 drops of a sodium benzophenone ketyl solution in THF. Stirring was continued for 0.5 h, after which time the solution was evaporated to dryness under vacuum, and the red residue was recrystallised from acetone/ethanol to give red crystals of $Ru_3(CO)_{10}(dppee)$ (0.61 g, 80%). Found (calcd.): C, 44.14 (44.13); H, 2.19 (2.25); P, 6.29 (6.33)%.

Preparation of $Ru_3(CO)_8(dppee)_2$

A solution of $Ru_3(CO)_{12}$ (0.52 g, 0.80 mmol) and dppee (0.65 g, 1.63 mmol) in benzene (40 cm³) was refluxed for 1 h. The resultant deep-red solution was evaporated to dryness under vacuum, and the red solid was recrystallised from acetone/ethanol to give red crystals of $Ru_3(CO)_8(dppee)_2$ (0.85 g, 80%). Found (calcd.): C, 53.95 (54.59); H, 3.21 (3.37); P, 9.13 (9.38)%.

Preparation of $\text{Ru}_3(\text{CO})_6(\text{dppee})_3$

This was prepared in a similar manner to $\text{Ru}_3(\text{CO})_8(\text{dppee})_2$, using a 3/1 molar ratio of dppee: $\text{Ru}_3(\text{CO})_{12}$, and 8 h reflux to give red crystals of $\text{Ru}_3(\text{CO})_6(\text{dppee})_3$ (76% yield). Found (calcd.): C, 60.15 (60.76); H, 4.20 (4.01); P, 10.87 (11.19)%.

Preparation of $\text{Os}_3(\text{CO})_{10}(\text{dppee})$

A solution of $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ (0.05 g, 0.52 mmol) in methanol (10 cm³) was added dropwise to a solution of $\text{Os}_3(\text{CO})_{12}$ (0.20 g, 0.22 mmol) and dppee (0.10 g, 0.26 mmol) in benzene (40 cm³) at 60°C. After stirring the solution for 1 h at 60°C, the orange solution was evaporated to dryness under vacuum and the orange residue was recrystallised from acetone/ethanol to give pale orange crystals of $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ (0.32 g, 95%). Found (calcd.): C, 34.32 (34.64); H, 1.85 (1.78); P, 4.82 (4.97)%.

Preparation of $\text{Os}_3(\text{CO})_8(\text{dppee})_2$

A mixture of $\text{Os}_3(\text{CO})_{12}$ (0.150 g, 0.16 mmol) and dppee (0.13 g, 0.33 mmol) in toluene (50 cm³) was heated under reflux for 9 h. The resulting orange solution was evaporated to dryness under vacuum. The orange residue was then separated by thin layer chromatography using a 2/1 mixture of petroleum ether (60–80°C): dichloromethane as eluant. Two bands were obtained, a minor green band (not characterised) and a major orange band which contained $\text{Os}_3(\text{CO})_8(\text{dppee})_2$ (0.15 g, 60%). Found (calcd.): C, 45.02 (45.36); H, 2.64 (2.80); P, 7.53 (7.80)%.

Crystal structure of $\text{Fe}(\text{CO})_3(\text{dppee}) \cdot 0.4\text{CH}_2\text{Cl}_2$

Red crystals of the solvated complex were grown from a dichloromethane/heptane solution and were found to be air-stable. A suitable crystal of approximate dimensions $0.4 \times 0.4 \times 0.3$ mm was found to be triclinic, space group $P\bar{1}$, a 14.106(2), b 10.683(1), c 9.387(1) Å, α 101.730(11), β 82.469(11), γ 94.505(10)°, V 1371 Å³, D_m 1.37, D_c 1.38 g cm⁻³, $Z = 2$, $\mu(\text{Mo-K}\alpha)$ 7.14 cm⁻¹. Intensity data were recorded on a Nonius CAD-4 diffractometer. The Fe atom was located by use of direct methods and the remaining atoms (other than hydrogen) were found by Fourier methods using the SHELX program [12], and using 4049 unique reflections with $|F| > 4\sigma(F)$. Least-squares refinement of positional and thermal parameters (anisotropic for Fe, P, and carbonyl C and O, isotropic for all other atoms), treating each phenyl ring as a rigid group, converged to an agreement factor R 6.3%. The atom coordinates are given in Table 4, and selected bond lengths and angles in Table 3. Tables of thermal parameters and lists of structure factors can be obtained from the authors on request.

Crystal structure of $\text{Os}_3(\text{CO})_{10}(\text{dppee})$

Orange crystals were grown from an acetone/ethanol solution, and a crystal of approximate dimensions $0.2 \times 0.3 \times 0.5$ mm was selected for study. The crystal was monoclinic, space group $P2_1/n$, a 12.782(2), b 12.494(3), c 23.905(4) Å, β 102.74(1)°, V 3724 Å³, D_c 2.15 g cm⁻³, $Z = 4$, $\mu(\text{Mo-K}\alpha)$ 104.18 cm⁻¹. Intensity data were recorded on a Nonius CAD-4 diffractometer. The osmium atoms were located by use of a Patterson map and the remaining atoms (other than hydrogen) were found by Fourier methods using the SHELX program [12], and using 5417 unique reflections with $|F| > 5\sigma(F)$. Least-squares refinement of positional and thermal

(anisotropic for Os, P, and O atoms, isotropic for all other atoms) parameters, treating each phenyl ring as a rigid group, converged to an agreement factor, R , of 12%. After absorption corrections by the method of Stuart and Walker [13], the agreement factor finally converged to $R = 8.5\%$. Selected bond lengths and angles are given in Table 5, and atom coordinates in Table 6. Tables of thermal parameters and lists of structure factors can be obtained from the authors on request.

Results and discussion

The reaction of $\text{Fe}(\text{CO})_5$ with dppee in the presence of Me_3NO produces two complexes which have been identified spectroscopically as $\text{Fe}(\text{CO})_4(\eta^1\text{-dppee})$ and $\text{Fe}(\text{CO})_3(\text{dppee})$. The infrared spectra of these complexes (Table 1) are similar to those of their bis(diphenylphosphino)methane (dppm) analogues [1,14]. In addition, the ^{31}P NMR spectra of these complexes are in agreement with a monodentate coordination and chelated coordination of the dppee ligand respectively (Table 2). No evidence for the formation of the dimeric complex $(\text{CO})_4\text{Fe}(\mu\text{-dppee})\text{Fe}(\text{CO})_4$ (analogous to the complex $(\text{CO})_4\text{Fe}(\mu\text{-dppm})\text{Fe}(\text{CO})_4$ formed as one of the products in the reaction of $\text{Fe}(\text{CO})_5$ with dppm [14]) was obtained, indicating that the dppee ligand has a surprisingly greater tendency to chelation, to form $\text{Fe}(\text{CO})_3\text{-(dppee)}$, than the dppm ligand.

TABLE 1

INFRARED DATA $\nu(\text{CO})$ (cm^{-1}) (CH_2Cl_2 solution)

Complex	
$\text{Ru}_3(\text{CO})_{10}(\text{dppee})$	2078m, 2005s, 1995sh, 1953m
$\text{Ru}_3(\text{CO})_8(\text{dppee})_2$	2040m, 1962vs, 1945sh, 1909w
$\text{Ru}_3(\text{CO})_6(\text{dppee})_3$	2060w, 2010w, 1925vs, 1880w, 1870sh
$\text{Fe}(\text{CO})_4(\text{dppee})$	2048s, 1972m, 1935vs,br
$\text{Fe}(\text{CO})_3(\text{dppee})$	1985s, 1910s,br
$\text{Os}_3(\text{CO})_{10}(\text{dppee})$	2090m, 2052s, 2025sh, 2006vs, 2000vs, 1970m, 1950m, 1940m
$\text{Os}_3(\text{CO})_8(\text{dppee})_2$	2040m, 1985sh, 1960vs, 1935m, 1897w

TABLE 2

 ^{31}P NMR DATA

Complex	$\delta(^{31}\text{P}\{^1\text{H}\})$ ^a
$\text{Os}_3(\text{CO})_{10}(\text{dppee})$	-8.66s
$\text{Os}_3(\text{CO})_8(\text{dppee})_2$	-0.98d ($J(\text{PP})$ 96 Hz) -3.84d ($J(\text{PP})$ 96 Hz)
$\text{Ru}_3(\text{CO})_{10}(\text{dppee})$	34.05s
$\text{Ru}_3(\text{CO})_8(\text{dppee})_2$	AA'BB' spectrum centred at 39.05
$\text{Ru}_3(\text{CO})_6(\text{dppee})_3$	37.55s
$\text{Fe}(\text{CO})_4(\text{dppee})$	79.74 (d, $J(\text{PP})$ 59 Hz) -10.84 (d, $J(\text{PP})$ 59 Hz)
$\text{Fe}(\text{CO})_3(\text{dppee})$	41.5s

^a Chemical shifts relative to 85% H_3PO_4 ; CD_2Cl_2 solution.

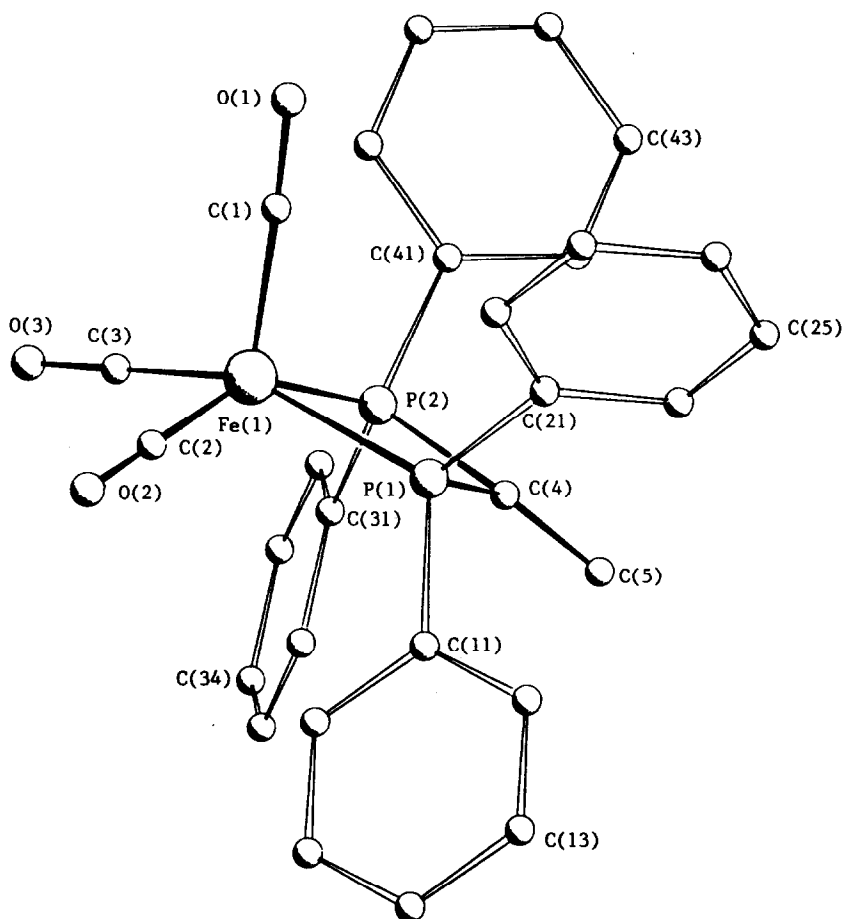


Fig. 1. Molecular structure of $\text{Fe}(\text{CO})_3(\text{dppee})$ with H atoms omitted.

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $\text{Fe}(\text{CO})_3(\text{dppee})$, WITH VALUES FOR THE FREE DPPEE LIGAND [8] GIVEN IN PARENTHESIS WHERE APPROPRIATE

Fe(1)–P(1)	2.221(1)	P(1)–C(4)	1.820(5) [1.829(4)]
Fe(1)–P(2)	2.221(1)	P(2)–C(4)	1.821(4) [1.838(4)]
Fe(1)–C(1)	1.784(5)	C(4)–C(5)	1.321(6) [1.327(6)]
Fe(1)–C(2)	1.753(7)	P(1)–C(11)	1.840(3) [1.837(4)]
Fe(1)–C(3)	1.757(5)	P(1)–C(21)	1.823(3) [1.827(6)]
C(1)–O(1)	1.141(6)	P(2)–C(31)	1.833(3) [1.838(5)]
C(2)–O(2)	1.161(9)	P(2)–C(41)	1.821(3) [1.819(6)]
C(3)–O(3)	1.167(7)		
C(1)–Fe(1)–C(2)	104.7(3)	P(1)–C(4)–P(2)	95.0(2) [119.0(3)]
C(1)–Fe(1)–C(3)	104.3(2)	P(1)–C(4)–C(5)	131.9(4) [124.7(3)]
C(1)–Fe(1)–P(1)	102.5(1)	P(2)–C(4)–C(5)	131.2(4) [116.1(4)]
C(1)–Fe(1)–P(2)	104.5(2)	Fe(1)–C(1)–O(1)	177.6(5)
P(1)–Fe(1)–P(2)	74.4(1)	Fe(1)–C(2)–O(2)	179.9(5)
P(1)–Fe(1)–C(2)	93.2(2)	Fe(1)–C(3)–O(3)	178.5(5)
C(2)–Fe(1)–C(3)	91.1(3)		
C(3)–Fe(1)–P(2)	87.8(2)		

TABLE 4

ATOMIC COORDINATES FOR $\text{Fe}(\text{CO})_3(\text{dppee}) \cdot 0.4\text{CH}_2\text{Cl}_2$

Atom	x	y	z
Fe(1)	0.2777(1)	0.0626(1)	0.6124(1)
P(1)	0.1952(1)	0.1688(1)	0.8122(1)
P(2)	0.2512(1)	-0.0720(1)	0.7669(1)
C(1)	0.3971(3)	0.1267(5)	0.6310(5)
O(1)	0.4740(3)	0.1675(4)	0.6377(5)
C(2)	0.2348(4)	0.1498(6)	0.4971(6)
O(2)	0.2060(4)	0.2089(6)	0.4226(5)
C(3)	0.2911(3)	-0.0715(6)	0.4691(5)
O(3)	0.3000(3)	-0.1622(5)	0.3763(5)
C(4)	0.1790(3)	0.0352(4)	0.9080(5)
C(5)	0.1180(3)	0.0126(5)	1.0204(5)
C(11)	0.0739(2)	0.2194(3)	0.8096(3)
C(12)	0.0293(2)	0.3097(3)	0.9219(3)
C(13)	-0.0644(2)	0.3403(3)	0.9167(3)
C(14)	-0.1134(2)	0.2807(3)	0.7991(3)
C(15)	-0.0687(2)	0.1904(3)	0.6868(3)
C(16)	0.0249(2)	0.1598(3)	0.6921(3)
C(21)	0.2516(2)	0.3027(3)	0.9308(3)
C(22)	0.3106(2)	0.3918(3)	0.8660(3)
C(23)	0.3538(2)	0.4965(3)	0.9534(3)
C(24)	0.3379(2)	0.5121(3)	1.1057(3)
C(25)	0.2789(2)	0.4230(3)	1.1705(3)
C(26)	0.2358(2)	0.3184(3)	1.0831(3)
C(31)	0.1768(2)	-0.2205(2)	0.7265(4)
C(32)	0.0833(2)	-0.2107(2)	0.6981(4)
C(33)	0.0242(2)	-0.3209(2)	0.6639(4)
C(34)	0.0587(2)	-0.4410(2)	0.6579(4)
C(35)	0.1522(2)	-0.4508(2)	0.6863(4)
C(36)	0.2112(2)	-0.3405(2)	0.7205(4)
C(41)	0.3523(2)	-0.1182(3)	0.8435(3)
C(42)	0.3471(2)	-0.1258(3)	0.9909(3)
C(43)	0.4269(2)	-0.1589(3)	1.0459(3)
C(44)	0.5118(2)	-0.1845(3)	0.9533(3)
C(45)	0.5169(2)	-0.1769(3)	0.8059(3)
C(46)	0.4372(2)	-0.1438(3)	0.7509(3)

The crystal structure of $\text{Fe}(\text{CO})_3(\text{dppee})$ was determined by X-ray diffraction methods. The molecular structure is shown in Fig. 1, selected bond lengths and angles are given in Table 3, and the atom coordinates in Table 4. The molecule consists of a distorted square-pyramidal structure in which the apex ligand is the carbonyl C(1)O(1). All four (apex ligand)-Fe-(basal ligand) angles are approximately equal, ranging from 102.5 – 104.7° , as required by ideal square-pyramidal geometry; but the four (basal ligand)-Fe-(basal ligand) angles are not equal (ranging from 74.4 – 93.2°) due to the steric constraints inherent in the dppee ligand. A comparison of the structure of $\text{Fe}(\text{CO})_3(\text{dppee})$ with that of the analogous dppm complex, $\text{Fe}(\text{CO})_3(\text{dppm})$ [15] shows that $\text{Fe}(\text{CO})_3(\text{dppee})$ is much closer to a square-pyramidal geometry since $\text{Fe}(\text{CO})_3(\text{dppm})$ has a structure intermediate between trigonal bipyramidal and square-pyramidal. For example, the four (apex

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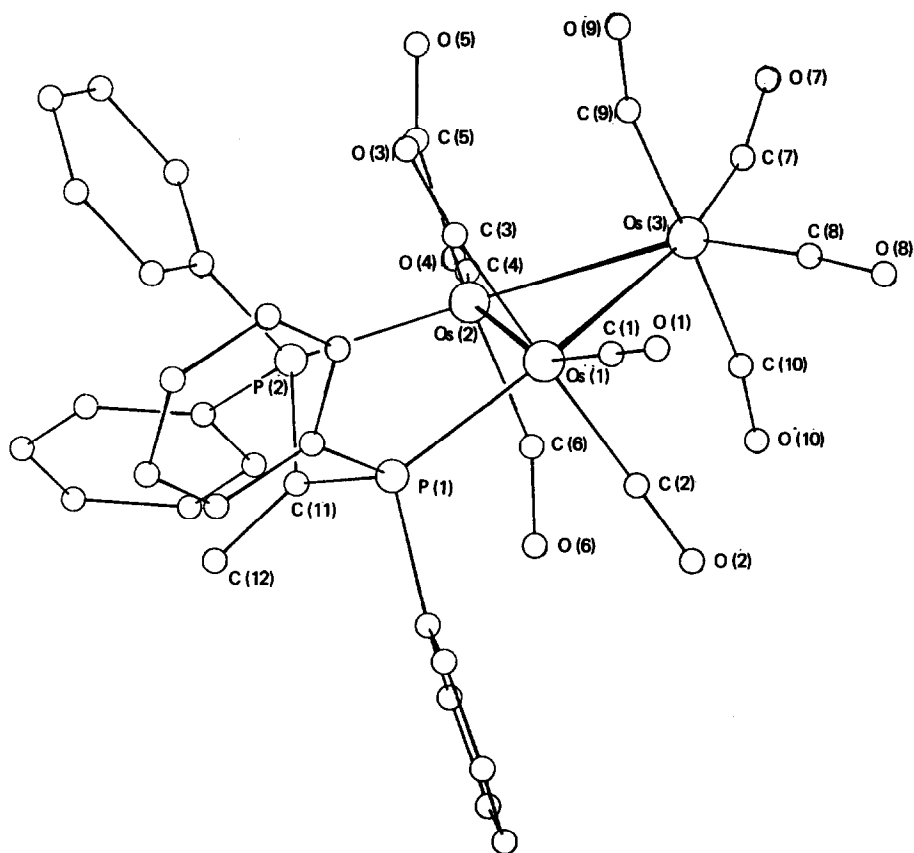


Fig. 2. Molecular structure of $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ with H atoms omitted

TABLE 5

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $\text{Os}_3(\text{CO})_{10}(\text{dppee})$

$\text{Os}(1)-\text{Os}(2)$	2.863(1)	$\text{Os}(2)-\text{C}(4)$	1.875(23)
$\text{Os}(1)-\text{Os}(3)$	2.864(1)	$\text{Os}(2)-\text{C}(5)$	1.910(19)
$\text{Os}(2)-\text{Os}(3)$	2.874(1)	$\text{Os}(2)-\text{C}(6)$	1.911(19)
$\text{Os}(1)-\text{P}(1)$	2.329(5)	$\text{Os}(3)-\text{C}(7)$	1.876(21)
$\text{Os}(2)-\text{P}(2)$	2.334(5)	$\text{Os}(3)-\text{C}(8)$	1.910(26)
$\text{P}(1)-\text{C}(11)$	1.810(21)	$\text{Os}(3)-\text{C}(9)$	1.939(28)
$\text{P}(2)-\text{C}(11)$	1.917(18)	$\text{Os}(3)-\text{C}(10)$	1.985(32)
$\text{C}(11)-\text{C}(12)$	1.486(32)	$\text{P}(1)-\text{C}(21)$	1.859(16)
$\text{Os}(1)-\text{C}(1)$	1.867(24)	$\text{P}(1)-\text{C}(31)$	1.855(13)
$\text{Os}(1)-\text{C}(2)$	1.905(21)	$\text{P}(2)-\text{C}(41)$	1.829(16)
$\text{Os}(1)-\text{C}(3)$	1.896(19)	$\text{P}(2)-\text{C}(51)$	1.813(14)
$\text{Os}(1)-\text{Os}(2)-\text{Os}(3)$	59.9(1)	$\text{Os}(2)-\text{Os}(1)-\text{P}(1)$	95.2(1)
$\text{Os}(2)-\text{Os}(1)-\text{Os}(3)$	60.2(1)	$\text{Os}(1)-\text{Os}(2)-\text{P}(2)$	89.5(1)
$\text{Os}(1)-\text{Os}(3)-\text{Os}(2)$	59.9(1)	$\text{P}(1)-\text{Os}(1)-\text{Os}(3)$	154.1(1)
$\text{P}(1)-\text{C}(11)-\text{P}(2)$	115.0(9)	$\text{P}(2)-\text{Os}(2)-\text{Os}(3)$	148.0(1)
$\text{P}(1)-\text{C}(11)-\text{C}(12)$	122.0(16)		
$\text{P}(2)-\text{C}(11)-\text{C}(12)$	117.1(16)		

TABLE 6

ATOMIC COORDINATES FOR $\text{Os}_3(\text{CO})_{10}(\text{dppe})$

Atom	x	y	z
Os(1)	0.1697(1)	0.0801(1)	0.3501(1)
Os(2)	0.2088(1)	0.2966(1)	0.3884(1)
Os(3)	0.3832(1)	0.1466(1)	0.4026(1)
P(1)	-0.0078(4)	0.1090(4)	0.3028(2)
P(2)	0.0241(4)	0.3249(4)	0.3720(2)
C(1)	0.1790(21)	-0.0685(19)	0.3446(10)
C(2)	0.2133(17)	0.0921(18)	0.2791(8)
C(3)	0.1355(15)	0.0744(16)	0.4233(7)
C(4)	0.2620(21)	0.4336(19)	0.4106(10)
C(5)	0.2286(18)	0.2764(18)	0.4692(8)
C(6)	0.2049(16)	0.3156(17)	0.3086(8)
C(7)	0.4945(17)	0.2294(18)	0.4459(9)
C(8)	0.4444(20)	0.0185(20)	0.3802(10)
C(9)	0.3528(23)	0.0820(22)	0.4711(10)
C(10)	0.4088(27)	0.2261(26)	0.3350(12)
O(1)	0.1817(18)	-0.1596(15)	0.3422(7)
O(2)	0.2493(16)	0.1024(15)	0.2383(7)
O(3)	0.1101(14)	0.0637(13)	0.4667(6)
O(4)	0.3002(19)	0.5188(14)	0.4195(9)
O(5)	0.2416(14)	0.2689(14)	0.5185(6)
O(6)	0.1972(17)	0.3384(14)	0.2609(7)
O(7)	0.5655(19)	0.2674(21)	0.4796(10)
O(8)	0.4760(19)	-0.0627(18)	0.3671(10)
O(9)	0.3438(17)	0.0373(21)	0.5128(9)
O(10)	0.4242(17)	0.2710(18)	0.2968(8)
C(11)	-0.0516(15)	0.2460(17)	0.3068(8)
C(12)	-0.1632(22)	0.2802(23)	0.2810(11)
C(21)	-0.0385(14)	0.0864(11)	0.2240(7)
C(22)	-0.0144(14)	0.1639(11)	0.1868(7)
C(23)	-0.0269(14)	0.1410(11)	0.1286(7)
C(24)	-0.0637(14)	0.0404(11)	0.1075(7)
C(25)	-0.0879(14)	-0.0371(11)	0.1447(7)
C(26)	-0.0753(14)	-0.0141(11)	0.2030(7)
C(31)	-0.1114(8)	0.0241(11)	0.3242(5)
C(32)	-0.0817(8)	-0.0478(11)	0.3695(5)
C(33)	-0.1602(8)	-0.1030(11)	0.3902(5)
C(34)	-0.2685(8)	-0.0862(11)	0.3655(5)
C(35)	-0.2982(8)	-0.0143(11)	0.3201(5)
C(36)	-0.2196(8)	0.0408(11)	0.2995(5)
C(41)	-0.0406(10)	0.2912(10)	0.4308(6)
C(42)	-0.0098(10)	0.3509(10)	0.4811(6)
C(43)	-0.0614(10)	0.3355(10)	0.5261(6)
C(44)	-0.1439(10)	0.2606(10)	0.5209(6)
C(45)	-0.1747(10)	0.2010(10)	0.4706(6)
C(46)	-0.1231(10)	0.2163(10)	0.4256(6)
C(51)	-0.0251(9)	0.4594(11)	0.3538(5)
C(52)	0.0353(9)	0.5243(11)	0.3255(5)
C(53)	0.0020(9)	0.6287(11)	0.3103(5)
C(54)	-0.0918(9)	0.6681(11)	0.3234(5)
C(55)	-0.1523(9)	0.6032(11)	0.3518(5)
C(56)	-0.1190(9)	0.4988(11)	0.3670(5)

ligand)–Fe–(basal ligand) angles in $\text{Fe}(\text{CO})_3(\text{dppm})$ range from 97.3–115.7° and the (basal ligand)–Fe–(basal ligand) angles range from 73.5–92.3°.

The crystal structure of the free dppee ligand has been recently determined [8]. A comparison of the bond lengths and angles in the free ligand (see Table 3) with those of the ligand in $\text{Fe}(\text{CO})_3(\text{dppee})$ shows that while the P–C and C=C bond lengths are not significantly altered on coordination of the ligand, the bond angles about the central carbon atom, C(4), which are not far from the expected 120° for an sp^2 carbon atom in the free ligand, are significantly distorted by the requirements of chelation to the iron atom. In particular, the P(1)–C(4)–P(2) angle is reduced to 95.0° upon chelation to iron. However, the sum of the angles at C(4) remains close to 360° (358.1°), as required for a trigonal planar carbon atom.

The dppee-substituted $\text{Ru}_3(\text{CO})_{12}$ complexes, $\text{Ru}_3(\text{CO})_{10}(\text{dppee})$, $\text{Ru}_3(\text{CO})_8(\text{dppee})_2$, and $\text{Ru}_3(\text{CO})_6(\text{dppee})_3$, are prepared in the same way as their dppm substituted analogues [1,16,17]. Spectroscopic data are given in Tables 1 and 2. The reaction of dppee with $\text{Os}_3(\text{CO})_{12}$, however, gives rise to $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ and $\text{Os}_3(\text{CO})_8(\text{dppee})_2$ only. No evidence for the formation of $\text{Os}_3(\text{CO})_9(\mu\text{-dppee})(\eta^1\text{-dppee})$ was obtained, in contrast to the analogous reaction with dppm in which $\text{Os}_3(\text{CO})_9(\mu\text{-dppm})(\eta^1\text{-dppm})$ is a major product [1]. This again indicates the enhanced tendency of the dppee ligand to chelation or bridging coordination.

The X-ray crystal structure of $\text{Os}_3(\text{CO})_{10}(\text{dppee})$ was determined. The molecular structure is shown in Fig. 2, selected bond lengths and angles are given in Table 5, and the atom coordinates in Table 6. As expected, the molecule consists of a triangle of osmium atoms, with the dppee ligand bridging one edge of the triangle, the phosphine groups occupying equatorial coordination sites. The dppee ligand in this complex has undergone much less distortion than in the complex $\text{Fe}(\text{CO})_3(\text{dppee})$. For example, the P(1)–C(11)–P(2) angle of 115° is close to the value found in the free ligand (119°). The sum of the angles at the central carbon atom, C(11), of the dppee ligand is again close to 360° (354°), indicating a planar, sp^2 -hybridised carbon atom. However, the carbon–carbon double bond C(11)–C(12) appears to have undergone a significant lengthening on coordination (1.49(3) Å compared to 1.327(6) Å in the free ligand). This is possible evidence for C=C activation on coordination, in agreement with the reactivity of coordinated dppee [6,7]; however the large estimated standard deviation for this bond length means that such evidence should be treated with caution. Apart from the complex $\text{Fe}(\text{CO})_3(\text{dppee})$ reported above, in the only crystal structure determination involving coordinated dppee ligands reported to date [7], in which the dppee ligands in $\text{ClAu}(\mu\text{-dppee})_2\text{AuCl}$ are bridging the two Au atoms, the carbon–carbon double bond length was found to be 1.326(9) Å, very close to the value found in the free ligand.

Acknowledgements

We thank the Isle of Man Government (J.A.C.) for a studentship, and Dr. M. Hursthouse (Queen Mary College, London) for the diffraction data collections.

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